Int J Thermophys (2009) 30:475–489
DOI 10.1007/s10765-008-0514-x

Effect of KCl and KNO_3 on Partial Molal Volumes and Partial Molal Compressibilities of Some Amino Acids at Different Temperatures

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Received: 13 March 2008 / Accepted: 16 September 2008 / Published online: 4 November 2008

Abstract Density (ρ) and ultrasonic velocity (u) values of amino acids L-alanine, L-proline, L-valine, and L-leucine in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions have been measured as a function of amino acid concentration at different temperatures (298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K, and 323.15 K). Using the ρ and u data, partial molal volume (ϕ_v^o) and partial molal isentropic compressibility (ϕ_k^o) values have been computed. The increase in partial molal volume with temperature has been attributed to the volume expansion of hydrated zwitterions. The ϕ_v^o and ϕ_k^o values of L-alanine, L-proline, L-valine, and L-leucine in 2 M aqueous KCl and KNO_3 solutions have been found to be larger than the corresponding values in water. The larger partial molal volumes of L-alanine, L-proline, L-valine, and L-leucine in 2 M aqueous KCl and KNO_3 solutions have been ascribed to the formation of 'zwitterion-$K^+/Cl^-/NO_3{}^-$' and '$K^+/Cl^-/NO_3{}^-$–water dipole' aggregates in solutions. The formation of these entities in solutions causes the release of water associated with zwitterions to the bulk water. The larger partial molal compressibilities of L-alanine-/L-proline-/L-valine-/L-leucine–2 M aqueous KCl/KNO_3 solutions than the corresponding values in water have been attributed to the formation of 'zwitterion–ion' and 'ion–water dipole' incompressible entities in solutions.

Keywords Amino acid · Partial molal isentropic compressibility · Partial molal volume · Salt · Zwitterion–ion interactions

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1 Introduction

Salt-induced electrostatic forces are known to play a vital role in modifying the protein structure by affecting properties like solubility, denaturation, and activity of enzymes [1,2]. Nandi and Robinson [3] studied the salting in/salting out effect of several salts on biological macromolecules and inferred that salts interact directly with the peptide group. The effects of electrolytes on the structure and function of proteins and nucleic acids in terms of their structure-making or structure-breaking property have been studied by a number of authors [1,2,4–11]. Due to the complex structure of proteins, a variety of different interactions with salts may occur, and it is difficult to resolve in a straightforward manner the various interactions participating in protein hydration. Therefore, to obtain more insight into the hydration of proteins and non-covalent forces stabilizing their native structure, it is necessary to determine the effects of salts on the model compounds of proteins such as amino acids and peptides.

A number of researchers have studied the partial molal volumes and partial molal isentropic compressibilities to investigate the interactions of amino acids with simple salts such as NH_4Cl, NaCl, KCl, Na_2SO_4, KSCN, $MgCl_2$, $CaCl_2$ [12–27], which act as stabilizers/destabilizers. Khoshbarchi et al. [28] have studied the ϕ_v^o and ϕ_k^o values of glycine in aqueous KCl and KNO_3 solutions. The observed behaviors of these properties were attributed to the formation of ion pairs between glycine and K^+, Cl^-, $NO_3{}^-$, and to the effects of the size difference of ions. Yasuda et al. [17] have reported data for ϕ_v^o and ϕ_k^o values for a number of amino acids in potassium chloride solutions. They explain the effect of potassium chloride on the ϕ_v^o and ϕ_k^o values of some amino acids in terms of hydration phenomena and electrostriction effects. The viscosity B-coefficient studies of glycine and L-alanine in 1:1 type of salts suggest that salts enhance the structure-making ability of amino acids [29].

The present work is a continuation of our research program on the thermodynamic studies of amino acids in aqueous salt solutions [30,31]. In this paper, the partial molal volumes and partial molal isentropic compressibilities of amino acids L-alanine, L-proline, L-valine, and L-leucine in 2 M aqueous KCl and KNO_3 solutions have been studied as functions of solute concentration and temperature (298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K, and 323.15 K) with a view to investigating the zwitterion–ion, zwitterion–water dipole, ion–water dipole, and ion–ion interactions operative in the systems.

2 Materials and Methods

The amino acids L-alanine, L-proline, L-valine, and L-leucine and the salts potassium chloride and potassium nitrate of high purity (≥99 %), used in the present studies, were purchased from SRL (India) and E. Merck (India), respectively. The amino acids were recrystallized twice in ethanol + water mixtures, dried at 383.15 K, and kept in a vacuum desiccator over P_2O_5 for at least 72 h before use. The salts were recrystallized twice in triply distilled water, dried at 423.15 K for at least 3 h, and then kept over P_2O_5 in a vacuum desiccator at room temperature for a minimum of 48 h prior to their use. Stock solutions of 2 M aqueous KCl and 2 M aqueous KNO_3 were prepared

in triply distilled water and were used as solvents for the preparation of amino acid solutions. The specific electrical conductivity of triply distilled water used was less than $18 \times 10^{-6}\,\Omega^{-1}\cdot\mathrm{cm}^{-1}$. All the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation. An ultrasonic interferometer (Mittal Model M-77, India) based on the variable-path principle was used for the measurement of the ultrasonic velocity at a frequency of 4 MHz at different temperatures using a method described elsewhere [32]. An average of 10 readings was taken as a final value of the ultrasonic velocity. Water from an ultra-thermostat (Type U-10) was circulated through the brass jacket surrounding the cell and the quartz crystal. The jacket was well insulated, and the temperature of the solution under study was maintained to an uncertainty of 0.01 °C. The instrument was calibrated with triple-distilled water. The ultrasonic velocity values of water at different temperatures were taken from the literature for calibration purposes [33]. The densities of solutions were measured with a pyknometer using a method described elsewhere [32]. The densities of pure water at various required temperatures were taken from the literature for calibration purposes [30]. The thermostated water bath used for measurements of ultrasonic velocity and the thermostated paraffin bath used for measurements of density were maintained at a desired temperature (±0.01 °C) for about 30 min prior to recording of readings at each temperature of study. Several very close readings of density calculated at each temperature were averaged.

The uncertainties in measurements of the ultrasonic velocity and density have been ascertained by comparing the measured values for water with corresponding literature values at different temperatures. For instance, the measured values of the ultrasonic velocity of water are found to be $1496.8\,\mathrm{m}\cdot\mathrm{s}^{-1}$, $1519.9\,\mathrm{m}\cdot\mathrm{s}^{-1}$, and $1536.4\,\mathrm{m}\cdot\mathrm{s}^{-1}$ at 298.15 K, 308.15 K, and 318.15 K, respectively (corresponding literature values [33] are $1496.687\,\mathrm{m}\cdot\mathrm{s}^{-1}$, $1519.808\,\mathrm{m}\cdot\mathrm{s}^{-1}$, and $1536.409\,\mathrm{m}\cdot\mathrm{s}^{-1}$); the experimental values of the density of water are $0.9971\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, $0.9942\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, $0.9903\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, and $0.9879\,\mathrm{g}\cdot\mathrm{cm}^{-3}$ at 298.15 K, 308.15 K, 318.15 K, and 323.15 K, respectively (corresponding literature values [34] are $0.997045\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, $0.994032\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, $0.990213\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, and $0.988036\,\mathrm{g}\cdot\mathrm{cm}^{-3}$). The uncertainties in the ultrasonic velocity and density measurements have been found to be within $0.2\,\mathrm{m}\cdot\mathrm{s}^{-1}$ and $0.1\,\mathrm{kg}\cdot\mathrm{m}^{-3}$, respectively.

3 Results and Discussion

The apparent molal volumes, ϕ_v, of amino acids L-alanine, L-proline, L-valine, and L-leucine have been calculated from the solution density values using the relation

$$\phi_\mathrm{v} = (M/\rho) - \{1000(\rho - \rho_\mathrm{o})/m\rho\rho_\mathrm{o}\} \tag{1}$$

where m is the molality ($\mathrm{mol}\cdot\mathrm{kg}^{-1}$) of the solution, M is the relative molar mass of the solute ($\mathrm{kg}\cdot\mathrm{mol}^{-1}$), and ρ_o and ρ are the density values ($\mathrm{kg}\cdot\mathrm{m}^{-3}$) of the solvent and solution, respectively. The density and ultrasonic velocity values are listed in Tables 1 and 2. The apparent molal volume values have been fitted by least squares with the linear equation

Table 1 Density values ($\rho \times 10^{-3}$, $kg \cdot m^{-3}$) as functions of solute concentration and temperature

Concentration ($mol \cdot kg^{-1}$)	Temperature (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
(i) L-*Alanine in 2 M aqueous KCl solution*						
0.0000	1.0891	1.0875	1.0856	1.0834	1.0809	1.0783
0.1857	1.0945	1.0934	1.0917	1.0896	1.0871	1.0844
0.3762	1.0988	1.0970	1.0950	1.0928	1.0904	1.0879
0.5714	1.1035	1.1015	1.0993	1.0971	1.0947	1.0922
0.7706	1.1094	1.1075	1.1054	1.1032	1.1008	1.0982
0.9751	1.1146	1.1132	1.1113	1.1092	1.1068	1.1040
1.1864	1.1212	1.1191	1.1169	1.1144	1.1118	1.1090
1.4044	1.1216	1.1197	1.1176	1.1155	1.1132	1.1108
(ii) L-*Alanine in 2 M aqueous* KNO_3						
0.0000	1.1229	1.1206	1.1180	1.1150	1.1118	1.1082
0.1802	1.1278	1.1255	1.1229	1.1200	1.1168	1.1132
0.3649	1.1318	1.1295	1.1269	1.1239	1.1206	1.1169
0.5543	1.1359	1.1330	1.1299	1.1267	1.1233	1.1198
0.7494	1.1388	1.1367	1.1342	1.1314	1.1282	1.1240
0.9499	1.1418	1.1393	1.1366	1.1338	1.1307	1.1275
1.1542	1.1466	1.1440	1.1412	1.1382	1.1349	1.1315
1.3650	1.1506	1.1476	1.1445	1.1413	1.1381	1.1347
(iii) L-*Proline in 2 M aqueous KCl solution*						
0.0000	1.0891	1.0875	1.0856	1.0834	1.0809	1.0783
0.1871	1.0922	1.0905	1.0887	1.0865	1.0841	1.0814
0.3813	1.0952	1.0935	1.0916	1.0895	1.0871	1.0844
0.5829	1.0984	1.0968	1.0949	1.0928	1.0905	1.0878
0.7925	1.1016	1.0999	1.0981	1.0960	1.0937	1.0911
1.0104	1.1048	1.1032	1.1013	1.0992	1.0969	1.0943
1.2376	1.1078	1.1062	1.1044	1.1024	1.1001	1.0976
1.4741	1.1109	1.1094	1.1076	1.1056	1.1033	1.1008
(iv) L-*Proline in 2 M aqueous* KNO_3 *solution*						
0.0000	1.1229	1.1206	1.1180	1.1150	1.1118	1.1082
0.1814	1.1258	1.1236	1.1211	1.1182	1.1149	1.1112
0.3694	1.1288	1.1266	1.1241	1.1212	1.1179	1.1143
0.5646	1.1317	1.1296	1.1271	1.1242	1.1209	1.1172
0.7673	1.1347	1.1326	1.1301	1.1272	1.1240	1.1204
0.9779	1.1377	1.1356	1.1331	1.1303	1.1271	1.1235
1.1969	1.1407	1.1386	1.1362	1.1333	1.1301	1.1265
1.4249	1.1437	1.1417	1.1392	1.1364	1.1332	1.1296
(v) L-*Valine in 2 M aqueous KCl solution*						
0.0000	1.0891	1.0875	1.0856	1.0834	1.0809	1.0783
0.0184	1.0895	1.0878	1.0859	1.0837	1.0813	1.0786
0.0369	1.0896	1.0881	1.0862	1.0841	1.0817	1.0791

Table 1 continued

Concentration ($mol \cdot kg^{-1}$)	Temperature (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
0.0554	1.0899	1.0883	1.0865	1.0844	1.0820	1.0794
0.0927	1.0906	1.0890	1.0871	1.0850	1.0827	1.0802
0.1303	1.0908	1.0894	1.0876	1.0856	1.0834	1.0809
0.1682	1.0913	1.0899	1.0883	1.0863	1.0842	1.0818
0.1873	1.0914	1.0901	1.0885	1.0867	1.0846	1.0822
(vi) L-*Valine in 2 M aqueous* KNO_3 *solution*						
0.0000	1.1229	1.1206	1.1180	1.1150	1.1118	1.1082
0.0178	1.1232	1.1209	1.1182	1.1153	1.1121	1.1086
0.0357	1.1235	1.1212	1.1186	1.1157	1.1124	1.1089
0.0537	1.1238	1.1215	1.1188	1.1159	1.1127	1.1092
0.0898	1.1246	1.1219	1.1191	1.1163	1.1133	1.1102
0.1264	1.1248	1.1225	1.1203	1.1176	1.1144	1.1107
0.1630	1.1251	1.1231	1.1206	1.1178	1.1146	1.1110
0.1814	1.1260	1.1234	1.1209	1.1180	1.1149	1.1115
(vii) L-*Leucine in 2 M aqueous KCl solution*						
0.0000	1.0891	1.0875	1.0856	1.0834	1.0809	1.0783
0.0184	1.0893	1.0877	1.0858	1.0836	1.0812	1.0785
0.0369	1.0896	1.0879	1.0860	1.0839	1.0815	1.0788
0.0555	1.0897	1.0882	1.0863	1.0842	1.0818	1.0792
0.0741	1.0899	1.0884	1.0866	1.0845	1.0821	1.0795
0.0928	1.0901	1.0886	1.0868	1.0848	1.0824	1.0798
0.1117	1.0904	1.0889	1.0871	1.0850	1.0827	1.0801
0.1306	1.0905	1.0890	1.0873	1.0852	1.0829	1.0803
(viii) L-*Leucine in 2 M aqueous* KNO_3 *solution*						
0.0000	1.1229	1.1206	1.1180	1.1150	1.1118	1.1082
0.0178	1.1230	1.1207	1.1181	1.1151	1.1119	1.1083
0.0358	1.1231	1.1208	1.1182	1.1153	1.1120	1.1085
0.0538	1.1232	1.1209	1.1184	1.1155	1.1122	1.1086
0.0719	1.1233	1.1211	1.1186	1.1157	1.1125	1.1089
0.0900	1.1235	1.1213	1.1188	1.1159	1.1126	1.1091
0.1083	1.1236	1.1214	1.1189	1.1160	1.1128	1.1093
0.1266	1.1238	1.1216	1.1191	1.1163	1.1131	1.1096

$$\phi_v = \phi_v^o + S_v m \tag{2}$$

where ϕ_v^o is the apparent molal volume at infinite dilution, which is also referred to as the partial molal volume of the solute, and S_v is the volumetric pairwise interaction coefficient [35,36]. ϕ_v^o values have been obtained by extrapolation of the linear plot of ϕ_v against molal concentration of the amino acid. A few data points well outside

Table 2 Ultrasonic velocity values (u, $\mathrm{m \cdot s^{-1}}$) as functions of solute concentration and temperature

Concentration ($\mathrm{mol \cdot kg^{-1}}$)	Temperature (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
(i) L-*Alanine in 2 M aqueous KCl solution*						
0.0000	1595.2	1605.9	1610.2	1616.4	1621.4	1626.5
0.1857	1609.8	1615.1	1622.7	1628.1	1634.2	1638.9
0.3762	1620.4	1625.4	1632.0	1637.0	1642.4	1648.0
0.5714	1630.2	1635.4	1640.7	1645.9	1650.4	1656.7
0.7706	1640.0	1644.4	1650.2	1656.2	1660.7	1665.0
0.9751	1649.8	1654.4	1660.6	1665.9	1670.1	1674.8
1.1864	1660.2	1664.2	1670.2	1675.8	1680.2	1685.4
1.4044	1670.4	1674.6	1680.4	1685.2	1690.4	1695.2
(ii) L-*Alanine in 2 M aqueous* KNO_3 *solution*						
0.0000	1562.0	1569.4	1575.8	1580.0	1584.6	1588.9
0.1802	1571.3	1577.3	1584.6	1589.2	1594.1	1598.3
0.3649	1582.4	1587.5	1594.0	1601.2	1605.2	1610.2
0.5543	1596.3	1602.0	1606.2	1613.6	1617.8	1622.0
0.7494	1607.6	1612.8	1616.9	1622.6	1627.0	1631.2
0.9499	1616.0	1621.0	1626.0	1631.7	1636.0	1641.7
1.1542	1625.0	1630.0	1635.2	1640.4	1645.2	1650.4
1.3650	1634.0	1639.5	1645.0	1650.3	1655.4	1660.5
(iii) L-*Proline in 2 M aqueous KCl solution*						
0.0000	1595.2	1605.9	1610.2	1616.4	1621.4	1626.5
0.1871	1608.0	1612.9	1618.9	1625.6	1630.0	1636.0
0.3813	1620.6	1625.9	1630.4	1637.2	1641.4	1646.4
0.5829	1631.8	1637.0	1642.0	1648.0	1652.6	1657.0
0.7925	1643.7	1649.0	1653.0	1660.0	1663.6	1669.0
1.0104	1654.0	1658.4	1664.0	1671.0	1675.0	1680.0
1.2376	1665.0	1671.0	1676.0	1683.0	1686.0	1691.0
1.4741	1676.0	1681.0	1688.0	1694.4	1698.0	1702.0
(iv) L-*Proline in 2 M aqueous* KNO_3 *solution*						
0.0000	1562.0	1569.4	1575.0	1580.0	1584.6	1588.9
0.1814	1575.6	1580.0	1584.0	1589.2	1594.0	1598.0
0.3694	1586.2	1592.0	1596.4	1600.4	1604.8	1608.0
0.5646	1600.4	1604.4	1608.0	1611.6	1615.0	1618.0
0.7673	1613.2	1616.8	1620.0	1623.2	1626.2	1629.2
0.9779	1625.2	1628.0	1632.0	1635.0	1638.0	1641.0
1.1969	1638.4	1641.0	1644.8	1648.0	1651.2	1654.0
1.4249	1650.4	1653.2	1657.2	1660.0	1664.0	1667.0
(v) L-*Valine in 2 M aqueous KCl solution*						
0.0000	1595.2	1605.9	1610.2	1616.4	1621.4	1626.5
0.0184	1599.2	1607.0	1613.2	1619.4	1626.2	1631.4
0.0369	1602.2	1610.2	1616.2	1622.8	1629.4	1634.4

Table 2 continued

Concentration ($mol \cdot kg^{-1}$)	Temperature (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
0.0554	1605.9	1613.2	1619.4	1626.0	1632.6	1637.4
0.0927	1612.0	1619.8	1626.0	1633.0	1639.2	1643.6
0.1303	1618.0	1626.2	1632.2	1639.2	1645.6	1650.0
0.1682	1624.0	1632.6	1638.0	1645.6	1651.8	1656.4
0.1873	1627.0	1636.0	1641.4	1649.0	1655.0	1659.6
(vi) L-*Valine in 2 M aqueous* KNO_3 *solution*						
0.0000	1562.0	1569.4	1575.0	1580.0	1584.5	1588.8
0.0178	1565.0	1572.6	1578.0	1583.0	1587.5	1592.0
0.0357	1568.0	1575.8	1581.2	1586.2	1590.5	1595.0
0.0537	1571.2	1578.8	1584.2	1589.4	1593.8	1598.0
0.0898	1574.4	1582.0	1587.2	1592.6	1597.0	1601.0
0.1264	1577.4	1585.0	1590.4	1595.8	1600.0	1604.2
0.1630	1580.6	1588.2	1593.6	1599.0	1603.2	1607.4
0.1814	1583.4	1591.4	1596.6	1602.0	1606.4	1610.6
(vii) L-*Leucine in 2 M aqueous KCl solution*						
0.0000	1595.2	1605.9	1610.2	1616.4	1621.4	1626.5
0.0184	1598.0	1607.2	1612.4	1619.0	1625.0	1630.0
0.0369	1601.4	1608.2	1615.6	1622.0	1628.6	1633.4
0.0555	1605.2	1612.0	1619.0	1626.0	1632.0	1637.0
0.0741	1608.0	1615.4	1622.4	1629.8	1635.4	1640.0
0.0928	1612.0	1619.8	1626.0	1633.2	1639.0	1644.0
0.1117	1616.0	1623.2	1629.4	1636.8	1642.6	1647.6
0.1306	1620.0	1627.0	1633.0	1640.2	1646.0	1651.0
(viii) L-*Leucine in 2 M aqueous* KNO_3 *solution*						
0.0000	1562.0	1569.4	1575.0	1580.0	1584.5	1588.8
0.0178	1566.4	1573.2	1579.2	1584.0	1588.4	1592.6
0.0358	1570.0	1577.4	1583.4	1588.2	1592.6	1596.4
0.0538	1574.2	1581.6	1587.6	1592.0	1596.4	1600.4
0.0719	1578.6	1585.2	1591.4	1596.4	1600.2	1604.8
0.0900	1582.4	1589.6	1595.2	1600.2	1604.6	1609.0
0.1083	1587.0	1593.4	1599.4	1604.6	1608.2	1613.0
0.1266	1591.0	1597.2	1603.4	1608.2	1612.4	1617.0

the precision of the measurements, particularly in the low concentration range, have been ignored in fitting the data with the relevant equation.

ϕ_v^o and S_v values are presented in Table 3. An examination of Table 3 reveals that the partial molal volume values of the amino acids, viz., L-alanine, L-proline, L-valine, and L-leucine, in 2 M aqueous solutions of KCl and KNO_3 at each temperature are higher than the corresponding values in an aqueous medium. The ϕ_v^o values are positive for all amino acids L-alanine, L-proline, L-valine, and L-leucine, in 2 M aqueous KCl

Table 3 Least-squares fit coefficients of equation $\phi_v = \phi_v^o + S_v m$ at different temperatures

Temperature (K)	$\phi_v^o \times 10^6$ ($m^3 \cdot mol^{-1}$)	$S_v \times 10^6$ ($m^3 \cdot mol^{-2} \cdot kg$)	$\sigma \times 10^6$ ($m^3 \cdot mol^{-1}$)
(i) L-*Alanine in 2 M aqueous KCl solution*			
298.15	60.64	0.658	0.8
303.15	59.55	0.145	1.0
308.15	60.00	−0.051	1.1
313.15	60.75	−0.044	1.2
318.15	59.91	0.118	1.2
323.15	59.78	0.342	1.0
(ii) L-*Alanine 2 M in aqueous* KNO_3 *solution*			
298.15	60.72	2.245	0.8
303.15	59.49	2.346	0.7
308.15	59.78	2.357	0.8
313.15	59.91	2.349	0.8
318.15	60.34	2.096	0.9
323.15	60.84	1.705	0.7
(iii) L-*Proline in 2 M aqueous KCl solution*			
298.15	91.58	−0.167	0.1
303.15	92.07	−0.493	0.1
308.15	91.97	−0.334	0.2
313.15	92.03	−0.362	0.1
318.15	91.79	−0.148	0.2
323.15	92.39	−0.536	0.2
(iv) L-*Proline in 2 M aqueous* KNO_3 *solution*			
298.15	89.57	−0.206	0.06
303.15	89.34	−0.032	0.02
308.15	89.17	0.198	0.09
313.15	89.02	0.405	0.17
318.15	89.61	0.082	0.09
323.15	90.15	−0.179	0.09
(v) L-*Valine in 2 M aqueous KCl solution*			
298.15	92.19	27.32	2.2
303.15	93.86	9.53	0.6
308.15	93.96	2.54	0.2
313.15	93.10	−0.04	0.8
318.15	90.10	8.54	0.7
323.15	92.51	−12.51	1.4
(vi) L-*Valine in 2 M aqueous* KNO_3 *solution*			
298.15	90.52	12.40	2.3
303.15	91.50	0.26	1.1
308.15	93.90	−11.50	2.0
313.15	90.65	4.65	1.9

Table 3 continued

Temperature (K)	$\phi_v^o \times 10^6$ ($m^3 \cdot mol^{-1}$)	$S_v \times 10^6$ ($m^3 \cdot mol^{-2} \cdot kg$)	$\sigma \times 10^6$ ($m^3 \cdot mol^{-1}$)
318.15	91.52	−2.10	1.4
323.15	88.09	14.58	1.4
(vii) L-*Leucine in 2 M aqueous KCl solution*			
298.15	110.39	5.000	0.9
303.15	111.43	−9.911	0.6
308.15	111.72	−19.375	0.6
313.15	110.66	−18.268	1.1
318.15	107.32	3.714	0.4
323.15	111.12	−30.000	1.3
(viii) L-*Leucine in 2 M aqueous* KNO_3 *solution*			
298.15	112.84	−12.206	0.3
303.15	113.17	−20.680	0.4
308.15	113.13	−26.301	0.6
313.15	113.37	−36.658	1.0
318.15	114.04	−37.226	0.7
323.15	113.72	−37.173	0.7

and 2 M aqueous KNO_3 solutions at all concentrations as well as at all temperatures, thereby showing the presence of strong solute–solvent interaction. The ϕ_v^o values for L-alanine, L-proline, L-valine, and L-leucine in 2 M KCl and 2 M KNO_3 solutions show an irregular trend. At neutral pH, amino acids exist as zwitterions. The electrostriction of water occurs near the end group of zwitterions. The presence of KCl and KNO_3 may affect the hydration spheres of charged end groups of zwitterions. As a result of K^+–COO^-, Cl^-–$NH_3{}^+$, and $NO_3{}^-$–$NH_3{}^+$ interactions, the hydrated zwitterions may relax water molecules to the bulk water which, in turn, may cause an increase in the volume. The increase in ϕ_v^o values with an increase in temperature may be attributed to the volume expansion of hydrated zwitterions of amino acids or a reduction in electrostriction. The increase in temperature might favor relaxing water molecules rather than binding to the charged end groups. The decrease in ϕ_v^o values for L-alanine, L-proline, L-valine, and L-leucine with temperature in the 2 M solutions of aqueous KCl and KNO_3 has been found to be insignificantly small.

A perusal of Table 3 reveals that the ϕ_v^o values for L-alanine in 2 M KCl and 2 M KNO_3 solutions at 298.15 K have been found to be 60.64 $cm^3 \cdot mol^{-1}$ and 60.72 $cm^3 \cdot mol^{-1}$, respectively, while in an aqueous medium it has been reported [37,38] to be 60.47 $cm^3 \cdot mol^{-1}$. The ϕ_v^o values for L-alanine in 0.5 m, 1.0 m, and 2.0 m aqueous NaCl at 298.15 K have been reported [39] to be (61.11 ± 0.07) $cm^3 \cdot mol^{-1}$, (62.26 ± 0.03) $cm^3 \cdot mol^{-1}$ and (63.21 ± 0.02) $cm^3 \cdot mol^{-1}$, respectively. The ϕ_v^o values for L-alanine in 0.0528 m and 0.1009 m $MgCl_2$ solutions at 298.15 K have been reported [18] to be (60.85 ± 0.06) $cm^3 \cdot mol^{-1}$ and (61.08 ± 0.27) $cm^3 \cdot mol^{-1}$, respectively, whereas in 0.3 m, 0.6 m, and 0.12 m aqueous DMSO solutions, the ϕ_v^o values have

been reported [39] to be $(60.18 \pm 0.03)\,\mathrm{cm^3 \cdot mol^{-1}}$, $(60.25 \pm 0.03)\,\mathrm{cm^3 \cdot mol^{-1}}$, and $(60.24 \pm 0.02)\,\mathrm{cm^3 \cdot mol^{-1}}$, respectively. The ϕ_v^o values for L-alanine in 6.0 m guanidine hydrochloride solution at 298.15 K has been reported [40] to be $(64.83 \pm 0.06)\,\mathrm{cm^3 \cdot mol^{-1}}$.

The ϕ_v^o values for L-proline in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions at 298.15 K have been found to be $91.58\,\mathrm{cm^3 \cdot mol^{-1}}$ and $89.56\,\mathrm{cm^3 \cdot mol^{-1}}$, respectively, whereas the ϕ_v^o value in an aqueous medium has been reported [41] to be $82.83\,\mathrm{cm^3 \cdot mol^{-1}}$. ϕ_v^o values for L-proline in 2.0 m aqueous LiCl and NaCl solutions at 298.15 K have been reported [17] to be $84.37\,\mathrm{cm^3 \cdot mol^{-1}}$ and $85.30\,\mathrm{cm^3 \cdot mol^{-1}}$, respectively.

The ϕ_v^o values for L-valine in 2 M aqueous KCl and 2 M aqueous KNO_3 at 298.15 K have been found to be $92.19\,\mathrm{cm^3 \cdot mol^{-1}}$ and $90.52\,\mathrm{cm^3 \cdot mol^{-1}}$, respectively, whereas it has been reported [42] to be $90.39\,\mathrm{cm^3 \cdot mol^{-1}}$ in an aqueous medium. The ϕ_v^o values for L-valine in 2.0 m aqueous glycerol solution at 298.15 K has been reported [43] to be $(91.47 \pm 0.04)\,\mathrm{cm^3 \cdot mol^{-1}}$, whereas in 2.0 m and 3.0 m aqueous NaCl solutions, the values have been reported [44] to be $(91.58 \pm 0.39)\,\mathrm{cm^3 \cdot mol^{-1}}$ and $(92.19 \pm 0.84)\,\mathrm{cm^3 \cdot mol^{-1}}$, respectively. The ϕ_v^o values for L-leucine in the 2 M aqueous KCl and 2 M aqueous KNO_3 solutions at 298.15 K have been found to be $110.39\,\mathrm{cm^3 \cdot mol^{-1}}$ and $112.83\,\mathrm{cm^3 \cdot mol^{-1}}$, respectively, whereas it has been reported [37] to be $107.74\,\mathrm{cm^3 \cdot mol^{-1}}$ in an aqueous medium. The ϕ_v^o for L-leucine in 1.0 m aqueous NaCl has been reported [12] to be $(108.40 \pm 0.38)\,\mathrm{cm^3 \cdot mol^{-1}}$, whereas in 6.0 m guanidine hydrochloride solutions at 298.15 K, it has been reported [40] to be $(110.72 \pm 0.11)\,\mathrm{cm^3 \cdot mol^{-1}}$. Because of the low solubility of L-valine and L-leucine in water, the solutions of these have been prepared in a lower concentration range than those for L-alanine and L-proline.

Franks et al. [45] showed that the partial molal volume of a non-electrolyte is a combination of the intrinsic volume, V_{int}, of the non-electrolyte and volume, V_s, due to its interactions with the solvent. The intrinsic volume is considered to be made up of two types of volumes, one Vander Waals volume, V_{vw}, and a void or empty volume, V_{void},

$$V_{\mathrm{int}} = V_{\mathrm{vw}} + V_{\mathrm{void}} \tag{3}$$

Shahidi et al. [46] modified this equation to include the contribution of interactions of a non-electrolyte solute with the solvent,

$$\phi_v^o = V_{\mathrm{vw}} + V_{\mathrm{void}} - n\sigma_s \tag{4}$$

where σ_s is the shrinkage in volume produced by the interactions of hydrogen bonding groups present in the solute with water molecules and n is the potential number of hydrogen bonding sites in the molecule. For electrolytes and zwitterionic solutes, the shrinkage is caused by electrostriction and ϕ_v^o can be evaluated as

$$\phi_v^o = V_{\mathrm{vw}} + V_{\mathrm{void}} - V_{\mathrm{shrinkage}} \tag{5}$$

V_{void} arises due to the thermal motion and packing effect, and $V_{\mathrm{shrinkage}}$ arises from interactions of the solute and the solvent. The $V_{\mathrm{shrinkage}}$ term will also incorporate

contributions associated with changes in solvent–solvent interactions that are consequences of interaction of the solvent with the solute. It is generally assumed that V_{vw} and V_{void} are approximately equal in water and in aqueous solutions, so that the positive volume of transfer for L-alanine, L-proline, L-valine, and L-leucine can be rationalized in terms of a decrease in the volume of shrinkage. In other words, some water molecules in the vicinity of the amino acids may be released to the bulk water in the presence of KCl and KNO_3 (Fig. 1). This brings about an increase in the volume of the solvent, thereby reducing the strong interactions between the amino acids and water. The slope, S_v, is a measure of solute–solute interactions. The trends of the variation of S_v with temperature in both solvents are irregular. The positive values of S_v for the studied amino acids in the 2 M KCl and 2 M KNO_3 solutions at all temperatures indicate the presence of stronger ion–ion and zwitterion–zwitterion interactions than those of apolar–apolar interactions, varying with the change of temperature, the nature of amino acids, and the nature of the solvent. The positive partial molal volumes for all amino acids at the experimental temperatures indicate the presence of strong K^+–COO^-, Cl^-–NH_3^+, and NO_3^-–NH_3^+ interactions at infinite dilution (as the ion–ion interactions vanish at infinite dilution). The negative value of S_v shows that the interactions are weak and less complex ion formation takes place.

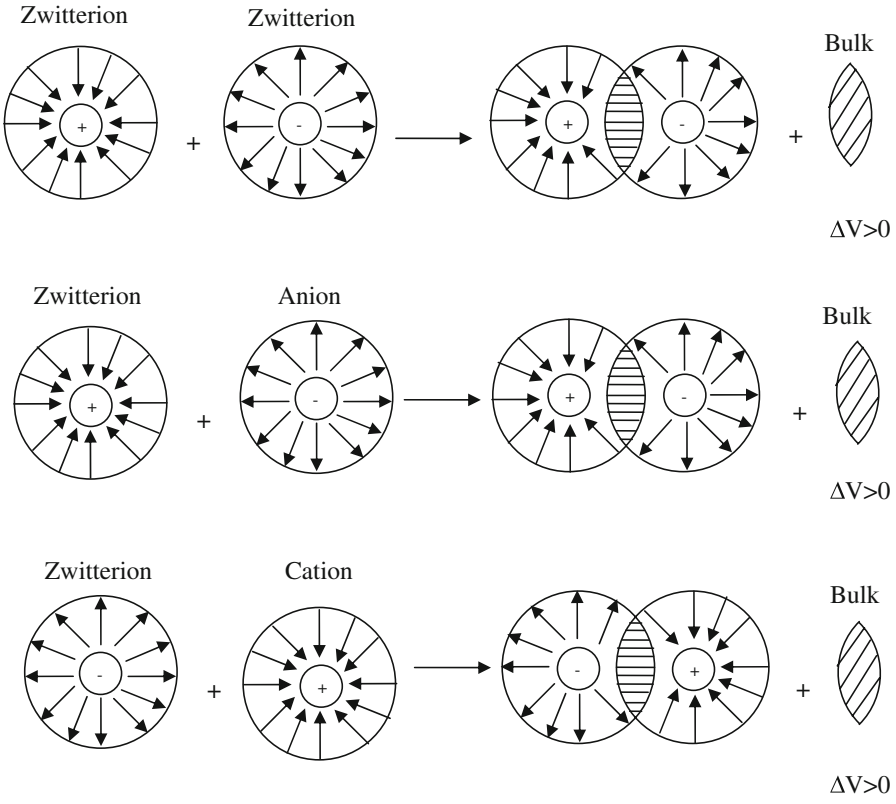

Fig. 1 Zwitterion–zwitterion and zwitterion–anion/cation interactions through the overlap of hydration cospheres and the resulting volume changes in aqueous salt solutions

The apparent molal isentropic compressibilities, ϕ_k, have been calculated using the relation

$$\phi_k = [\{1000(\kappa_s - \kappa_o)\}/m\rho_o] + \kappa_s\phi_v \tag{6}$$

In the above equation, m is the molality of the solution ($mol \cdot kg^{-1}$), ρ_o is the density of the solvent ($kg \cdot m^{-3}$), and $\kappa_s(= 1/(\rho u^2))$ and $\kappa_o(= 1/\rho_0 u_0^2)$ are the isentropic compressibilities of the solution and solvent ($m^2 \cdot N^{-1}$), respectively. The values of ϕ_k have been fitted by least squares with the equation

$$\phi_k = \phi_k^o + S_k m \tag{7}$$

where ϕ_k^o is the apparent molal isentropic compressibility at infinite dilution, which is also referred to as the partial molal isentropic compressibility, and is a measure of solute–solvent interactions.

The ϕ_k^o and S_k values have been listed in Table 4. The partial molal isentropic compressibilities of L-alanine in the 2 M aqueous KCl and 2 M aqueous KNO_3 solvents at 298.15 K have been found to be -1.995×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$ and 5.106×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$, respectively. The ϕ_k^o value for L-alanine in an aqueous medium at 298.15 K has been reported to be -2.556×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$ [37]. The ϕ_k^o values for L-proline in 2 M aqueous KCl and 2 M aqueous KNO_3 solvents at 298.15 K have been found to be 0.886×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$ and 0.777×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$, respectively ($-2.325 \times 10^{-11}$ $bar^{-1} \cdot m^3 \cdot mol^{-1}$ in the aqueous medium) [37]. The ϕ_k^o values for L-valine in the two electrolytic solutions at 298.15 K have been found to be -0.578×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$ and -3.66×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$, respectively ($-3.0 \times 10^{-11}$ $bar^{-1} \cdot m^3 \cdot mol^{-1}$ in the aqueous medium [47]), whereas they are -2.075×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$ and -5.566×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$, respectively, for L-leucine at 298.15 K (-3.178×10^{-11} $bar^{-1} \cdot m^3 \cdot mol^{-1}$ in an aqueous medium) [37]. The ϕ_k^o values, either negative or positive, are of smaller magnitude in all the systems studied here. The bulk water which has an open structure becomes electrostricted water, i.e., a less compressible state of water on the addition of KCl and KNO_3 and this accounts for the higher partial molal compressibilities for the amino acids in 2 M aqueous KCl and KNO_3 solutions than the corresponding values in water. The ϕ_k^o values for the L-alanine and L-proline in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions and for L-valine and L-leucine in 2 M aqueous KCl are higher than the corresponding values in an aqueous medium, whereas for L-valine and L-leucine in 2 M aqueous KNO_3 solutions, the ϕ_k^o values are quite close to the corresponding values in an aqueous medium. Similar trends have been reported by Yasuda et al. [17] for some amino acids in 2 m aqueous LiCl, NaCl, and KCl solutions. These values apparently indicate a larger ordering effect of the solute molecules in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions.

A simple model [37] can be used to express the partial molal isentropic compressibility of the amino acid as

$$K_s^0 = K_s^0(\text{int}) + K_s^0(\text{elect}) \tag{8}$$

Table 4 Least-squares fit coefficients of equation $\phi_k = \phi_k^o + S_k m$ at different temperatures

Temperature (K)	$\phi_k^o \times 10^{11}$ ($bar^{-1} \cdot m^3 \cdot mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1} \cdot m^3 \cdot mol^{-2} \cdot kg$)	$\sigma \times 10^{11}$ ($bar^{-1} \cdot m^3 \cdot mol^{-1}$)
(i) L-*Alanine in 2 M aqueous KCl solution*			
298.15	−1.99	5.56	1.68
303.15	8.05	−1.31	0.40
308.15	2.97	2.88	1.45
313.15	4.64	1.69	1.13
318.15	6.89	−0.25	0.59
323.15	3.77	2.39	1.69
(ii) L-*Alanine in 2 M aqueous* KNO_3 *solution*			
298.15	5.11	−1.41	1.70
303.15	8.28	−3.46	2.12
308.15	6.21	−1.14	0.79
313.15	5.17	−0.48	1.47
318.15	5.36	−0.56	1.13
323.15	5.30	−0.73	1.17
(iii) L-*Proline in 2 M aqueous KCl solution*			
298.15	0.89	0.23	0.02
303.15	1.92	−0.48	0.23
308.15	1.72	−0.34	0.11
313.15	1.64	−0.29	0.08
318.15	1.74	−0.33	0.10
323.15	1.65	−0.24	0.05
(iv) L-*Proline in 2 M aqueous* KNO_3 *solution*			
298.15	0.78	0.04	0.07
303.15	1.20	−0.19	0.07
308.15	1.50	−0.39	0.12
313.15	1.52	−0.35	0.07
318.15	1.56	−0.32	0.03
323.15	1.68	−0.38	0.02
(v) L-*Valine in 2 M aqueous KCl solution*			
298.15	−0.57	−20.49	2.78
303.15	2.75	−36.20	1.67
308.15	1.46	−30.72	2.01
313.15	1.42	−32.10	2.09
318.15	0.32	−27.42	2.47
323.15	0.47	−27.11	2.36
(vi) L-*Valine in 2 M aqueous* KNO_3 *solution*			
298.15	−3.66	15.89	0.36
303.15	−4.02	17.90	0.39
308.15	−3.64	15.97	0.39
313.15	−3.66	15.52	0.38

Table 4 continued

Temperature (K)	$\phi_k^o \times 10^{11}$ ($bar^{-1} \cdot m^3 \cdot mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1} \cdot m^3 \cdot mol^{-2} \cdot kg$)	$\sigma \times 10^{11}$ ($bar^{-1} \cdot m^3 \cdot mol^{-1}$)
318.15	−3.36	14.18	0.38
323.15	−3.63	16.41	0.37
(vii) L-*Leucine in 2 M aqueous KCl solution*			
298.15	−2.07	−11.58	0.25
303.15	3.10	−48.43	1.32
308.15	−3.84	12.59	1.30
313.15	−1.50	−14.56	0.36
318.15	−3.74	3.69	0.18
323.15	−3.21	0.18	0.11
(viii) L-*Leucine in 2 M aqueous* KNO_3 *solution*			
298.15	−5.56	3.96	0.32
303.15	−4.80	−0.34	0.18
308.15	−5.57	6.54	0.06
313.15	−4.91	0.36	0.09
318.15	−4.79	3.44	0.26
323.15	−4.17	−5.29	0.11

where K_s^0(int) is the intrinsic partial molal isentropic compressibility of the amino acid and K_s^0(elect) is the electrostriction partial molal isentropic compressibility due to hydration of the amino acid. The K_s^0(int) for the amino acids can be assumed to be almost zero as the value of K_s^0(int) is expected to be very small [37]. Thus, K_s^0 may be considered to represent K_s^0(elect). The reported K_s^0 values for all the amino acids in water are negative. The negative values of K_s^0 seem to result from the hydration of the charged centers of the amino acids, as the hydrated water appear to be less compressible than bulk water. The values of S_k for all systems under study are found to be negative, which suggest the presence of essentially weak zwitterion–zwitterion interactions in the systems.

Acknowledgments The authors are thankful to the Chairman, Department of Chemistry, A.M.U. Aligarh, for providing the necessary facility required in this research project. One of the authors (I.K.) thanks UGC for awarding the UGC fellowship.

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